BENEFICIATION OF COAL BY OXYGEN REMOVAL

FINAL REPORT

BY

SNC INC.

TECHNICAL DEVELOPMENT DEPARTMENT

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ABSTRACT

Four low rank Canadian coals, namely, Bienfait, Sundance, Onakawana and Forestburg were hydrothermally treated with the aqueous solution of $FeSO_4$ to remove oxygen from them. The Bienfait coal was treated with the $FeSO_4$ solution in different concentrations at the temperature of 100°C and 150°C to establish the "best" process conditions for the reaction temperature and catalyst concentration. The reaction temperature of 100°C with a $FeSO_4$ solution concentration of 1.6 g/250 ml were determined to be the best process conditions. Thirty-six percent of the oxygen was removed from Bienfait lignite at these conditions. Two other salts of iron, namely, $FeCl_2$ and $Fe(OAC)_2$ were tested as catalysts. $FeSO_4$ was judged to be the most active catalyst followed by $Fe(OAC)_2$ and $FeCl_2$ respectively in terms of their activity. The remaining three coals were treated at the same process conditions of temperature and catalyst concentration. The amount of oxygen removal was greatest for Forestburg coal and least for Sundance coal. The calorific values of the treated samples were determined. The calorific values of the treated Onakawana and Sundance coal samples were higher than the calorific values of original coals, indicating the increase in the fuel value of coal after the treatment.

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1.0 INTRODUCTION

The elemental constituents of coal are carbon, hydrogen, nitrogen, sulfur and oxygen. The amount of these constituents vary with the rank of coal. The percentage of oxygen decreases as the rank of the coal increases. Figure 1.1, redrawn from D.D. Whitehurst et al.(1) depicts the general relationship by which the various oxygen functional groups found in coals decrease as the rank of coal increases.

Oxygen in coal lowers its fuel value and hence, lowers its commercial value. If coal is to be liquefied by hydrogenation, the oxygen present has also to be hydrogenated. The end product, in this case, is water which has no fuel value. In essence, the hydrogen is wasted if it is used to remove oxygen from coal.

Thus, a process for removal of oxygen from coal would be beneficial in terms of:

- improving the economics of utilizing low-grade fuels such as lignite or peat;
- decreasing the costly hydrogen consumption in coal liquefaction processes.

This work is a continuation of the project titled "Investigation to Develop or Innovate Methods for the Removal of Oxygen from Coals", Phase II, carried out for CANMET. In that investigation, several inorganic reducing agents of various chemical characteristics had been tested to find out if the oxygen content of coal could be reduced. It was found that $FeSO_4$ catalytically deoxygenated both lignite and bituminous coals. The present investigation was undertaken to treat four Canadian coals of different ranks with three different salts of iron, namely; $FeSO_4$, $Fe(OAC)_2$ and $FeCl_2$. In the first part of the

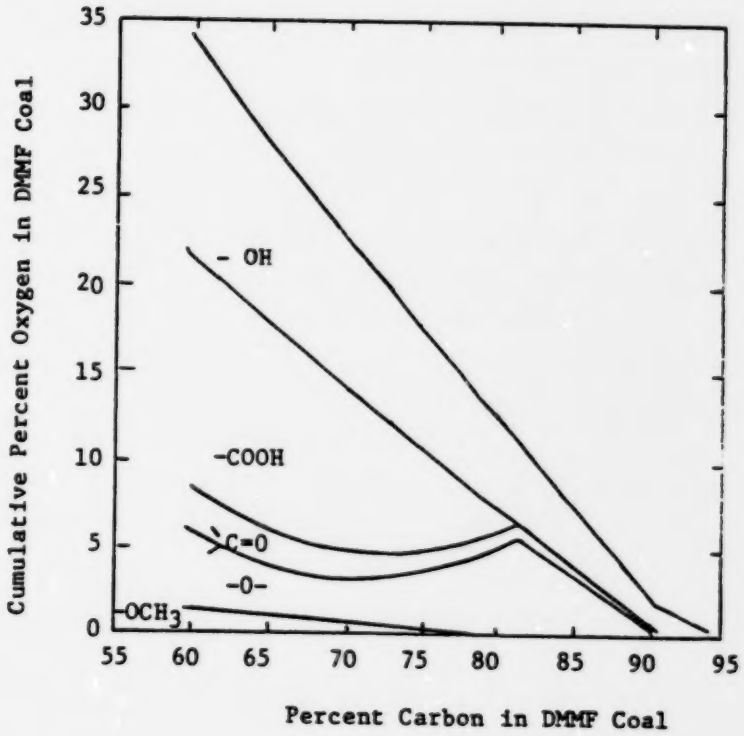

Figure 1.1 Distribution of Oxygen Functionality in Coals

work, Bienfait coal was treated with the $FeSO_4$ solution in different concentrations at the temperatures of 100°C and 150°C to establish the "best" process conditions for reaction the temperature and the catalyst concentration. At the "best" conditions, Bienfait coal was treated with two other iron salts. A total of 13 runs were made to establish the "best" reaction temperature, and the catalyst concentration which was most effective. The remaining three coals were treated at the "best" condition. As will be noted, the tests were carried out at preselected temperatures and concentrations. The "best" conditions were those conditions which resulted in the greatest removal of oxygen from Bienfait lignite using $FeSO_4$ as the catalyst. Even better conditions might have been found if the search grid had been made finer. These same "best" conditions of catalyst concentration and temperature were used in testing other coals and other catalysts. Other process conditions might have been still better for these other coals and catalysts. The experimental work was carried out at the Technitrol Laboratories Ltd. located at Dorval, Quebec.

2.0 EXPERIMENTAL

2.1 Coals Selection

Four Canadian coals, each having a different oxygen content, were selected for the present investigation. The coals tested were Bienfait coal from Saskatchewan, Sundance from Alberta, Onakawana from Ontario and Forestburg coal from Alberta.

2.2 Coal Sample Preparation

Master samples were crushed and ground to a particle size of about 125 μm. After screening with 80 mesh screen, each powdered coal sample was stored under a CO_2 atmosphere in a closed plastic container.

2.3 Catalyst Selection

In the previous investigation, it had been demonstrated that ferrous sulphate had the ability to catalytically remove oxygen from coal, probably by decarboxylation. It was of interest to know if other ferrous salts behaved in the same manner. Since pH of the solution or the anion might play some role in the catalytic effect, two very different ferrous salts were also tested as well as ferrous sulphate. Ferrous acetate is the salt of a weak organic acid, and ferrous chloride is the salt of a strong inorganic acid.

2.4 Experimental Program

The experimental program was divided into two phases. Phase I was to determine the "best" conditions of catalyst concentration and temperature using ferrous sulphate as the catalyst and Bienfait lignite as the test coal. Two series of tests were carried out in Phase I. One series at 100°C, the other at 150°C. In each series, the catalyst concentration was varied stepwise at the following concentrations: 0, 2, 6.4, 20,

2.4 Experimental Program (cont'd)

60, and 200 grams of catalyst/litre. The amount of oxygen removed at each set of conditions was determined. The largest decrease in oxygen content was found at 100°C and a catalyst concentration of 6.4 grams/litre. These experimental conditions were then selected for further work. They are referred to as the "best" conditions, henceforth, although clearly there maybe somewhat better conditions at a temperature and catalyst concentration slightly removed from these conditions. The other ferrous salts were tested at these same conditions. Again, the effect may have been better at some other conditions in the close vicinity.

Other coals were tested at the same "best" conditions. In this case, it is even more likely that better results would have been observed at other conditions. However, recognizing that this investigation was designed to screen various catalysts and coals, the use of the approxima "best" conditions was justified.

2.5 Experimental Scheme

The experimental scheme presented in Figure 2.1 shows the sequence of experimental steps. The experimental equipment consisted of an autoclave with a nominal capacity of 1 litre. The autoclave was equipped with a stirrer and the samples were continuously stirred during the run. The temperature of the content of the autoclave was measured by thermocouple and was read on the digital Digimite temperature indicator.

The 50 g ground sample of coal, along with demineralized water (blank run) or with an aqueous solution containing a particular catalyst, was placed in a stainless steel container. The container was placed in the

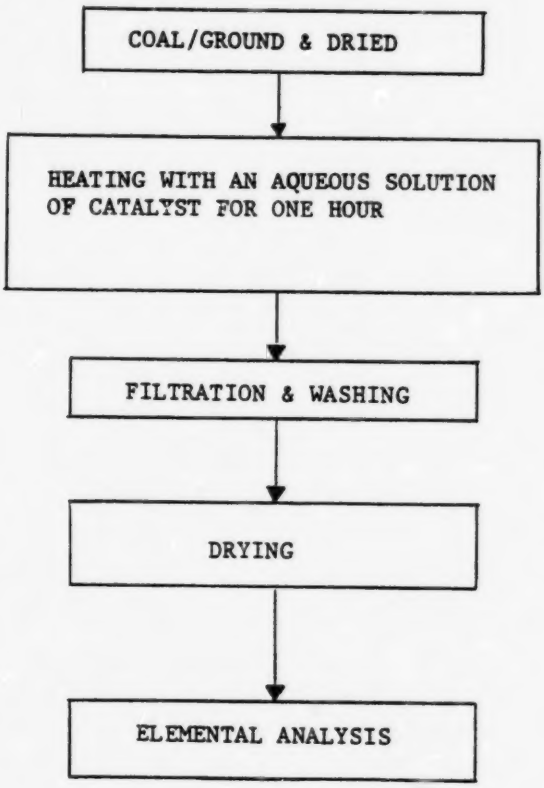

Figure 2.1 Coal Treatment Scheme

2.5 Experimental Scheme (cont'd)

autoclave. The autoclave was heated by electric heating coils wound around outside. The temperature was controlled manually. Thus, when the autoclave temperature reached the specified degree (100°C or 150°C), the heating was turned off. There was no problem in controlling the temperature within $\pm$ 2°C. The autoclave content was continuously stirred for one hour. The sample was filtered using a buchner funnel. The residue remaining on the filter paper was washed thoroughly to remove any adhering iron salts. The residue was dried under vacuum for one hour at 110°C. The dried sample was stored in tightly capped glass sample bottles. The dry residue was then analyzed for ash, C, H, N, S, and O (by difference). The calorific value of the sample was determined by ASTM D2015-66 method. A total of 24 runs were carried out. The conditions for the runs are shown in Table 2-1.

Table 2-1: Experimental Runs

RUN NO.	COAL	CATALYST	CONCENTRATION g/250 ml	TEMPERATURE
11	Bienfait	None	Blank	100°C
21	Bienfait	$FeSO_4$	50	100°C
31	Bienfait	$FeSO_4$	15	100°C
41	Bienfait	$FeSO_4$	5	100°C
51	Bienfait	$FeSO_4$	1.6	100°C
221	Bienfait	$FeSO_4$	0.5	100°C
61	Bienfait	None	Blank	150°C
71	Bienfait	$FeSO_4$	50	150°C
81	Bienfait	$FeSO_4$	15	150°C
91	Bienfait	$FeSO_4$	5	150°C
101	Bienfait	$FeSO_4$	1.6	150°C
111	Bienfait	$FeCl_2$	"best", 1.6	"best", 100
121	Bienfait	$Fe(OAC)_2$	"best" 1.6	"best", 100
132	Sundance	None	Blank	100°C
142	Sundance	$FeSO_4$	1.6	100°C
152	Sundance	$FeSO_4$	0.5	100°C
163	Onakawana	None	Blank	100°C
173	Onakawana	$FeSO_4$	1.6	100°C
183	Onakawana	$FeSO_4$	0.5	100°C
194	Forestburg	None	Blank	100°C
204	Forestburg	$FeSO_4$	1.6	100°C
214	Forestburg	$FeSO_4$	0.5	100°C
233	Onakawana	$FeSO_4$	0.5	150°C
244	Forestburg	$FeSO_4$	0.5	150°C

3.0 RESULTS AND DISCUSSION

3.1 General

The results of the analyses are shown in Tables 3.1 to 3.8. Table 3.1 shows analysis of the four Canadian coals tested. Table 3.2 contains the results of deoxygenation treatment for Bienfait lignite. Table 3.3 presents deoxygenation results using three different catalysts. Tables 3.4 to 3.6 show deoxygenation results for Sundance coal, Onakawana lignite and Forestburg coal respectively. The heating values of the treated coal samples and value appreciation of coal are given in Tables 3.7 and 3.8 respectively.

The reaction mechanism proposed in the report is subject to confirmation in further investigations. Due to the constraints on the time and funds available, the detailed reaction mechanism study could not be carried out but the catalytic oxygen removal capability of the aqueous $FeSO_4$ solution has been established and confirmed.

3.2 Results - Phase I

The "best" process conditions viz temperature and catalyst concentration were determined. A previous study (2) had established that oxygen removal takes place at 150°C. A temperature of 100°C was chosen to determine the lower reaction temperature. Eleven runs were carried out to determine these conditions. Six runs were made at 100°C (Run Nos. 11, 21, 31, 41, 51 and 221) and five runs were carried out at 150°C (Run Nos. 61, 71, 81, 91 and 101). Two more runs (Run Nos. 111 and 121) were carried out utilizing $FeCl_2$ and $Fe(OAC)_2$ as catalysts at the "best" temperature and catalyst concentration.

3.2.1 Effect of Catalyst Concentration

The results of Run Nos. 21, 31, 41, 51 and 221 carried out with the declining concentration of $FeSO_4$ solution at 100°C are shown in Table 3.2.

Table 3.1 Ultimate Analysis of Coals Tested
Basis: Moisture Free

Type of Coal	Bienfait	Sundance	Forestburg	Onakawana
Ultimate Analysis %				
Ash	11.88	14.60	9.50	36.65
C	63.15	63.30	64.00	44.92
H	3.76	3.90	3.90	2.54
N	1.22	0.80	1.70	0.95
S	0.57	0.30	0.60	1.06
O (diff)	19.43	17.10	20.30	13.88

Table 3.2 Deoxygenation Results for Bienfait Lignite
Basis: Mositure Free

Run No.	Type of Coal	Catalyst	Temp. °C	Conc.of Catalyst g/250 ml	Ultimate Analysis, %						Atomic Ratios	
					Ash	C	H	N	S	O(Diff)	O/C	H/C
01	Bienfait	-	-	-	11.88	63.15	3.76	1.22	0.57	19.43	0.231	0.714
11	Bienfait	$FeSO_4$	100	-	12.86	58.09	3.84	0.62	0.47	24.12	0.311	0.793
21	Bienfait	$FeSO_4$	100	50	11.34	67.93	4.40	0.85	0.66	14.83	0.164	0.777
31	Bienfait	$FeSO_4$	100	15	14.60	65.38	4.30	1.24	0.66	13.82	0.158	0.789
41	Bienfait	$FeSO_4$	100	5	13.92	63.97	3.78	1.19	0.52	16.53	0.194	0.710
51	Bienfait	$FeSO_4$	100	1.6	13.53	67.56	4.43	0.70	0.56	14.35	0.147	0.787
221	Bienfait	$FeSO_4$	100	0.5	11.27	62.62	3.92	1.59	0.61	19.98	0.239	0.751
61	Bienfait	$FeSO_4$	150	-	13.75	65.15	4.00	1.34	0.67	15.10	0.174	0.737
71	Bienfait	$FeSO_4$	150	50	11.91	63.41	3.97	1.18	0.76	18.78	0.222	0.751
81	Bienfait	$FeSO_4$	150	15	12.93	62.04	3.79	0.84	0.97	19.43	0.235	0.733
91	Bienfait	$FeSO_4$	150	5	14.33	61.96	3.73	1.11	0.58	18.29	0.221	0.722
101	Bienfait	$FeSO_4$	150	1.6	12.45	64.47	4.25	0.75	0.55	17.53	0.204	0.791

3.2.1 Effect of Catalyst Concentration (cont'd)

In the blank Run No. 11, the percentage of carbon content has gone down while the hydrogen and oxygen content has gone up. It was assumed in the analysis of the data that the ash is not affected by the treatment with water. The organic matter per unit amount of ash was determined for original coal and the coal after blank run. It was determined that about 8.5% of organic material in coal was dissolved (or lost) by merely heating it with water at 100°C. It is believed that this is because of dissolution of humic acids of coal in water. The sample calculations are shown in Appendix B. The rise in hydrogen and oxygen content of coal after treatment is due to the hydrolysis of the ester linkages in coal. There may be two reactions taking place simultaneously during the hydrothermal treatment.

- Hydrolysis of the ester groups in coal
- Catalytic oxygen removal by decarboxylation.

The hydrolysis reaction fixes one atom of oxygen and two atoms of hydrogen for every molecule of ester hydrolysed. The decarboxylation removes oxygen by evolving CO_2, thus for every two atoms of oxygen removed, one atom of carbon is removed. Hence, when decarboxylation takes place, H/C atomic ratio of the material should increase. Assuming that only decarboxylation is taking place in the treatment, the loss of carbon atoms was estimated and new H/C ratio was determined for the runs (the sample calculations are shown in Appendix A). The increase in the H/C ratio only due to carbon loss because of decarboxylation is low as compared to the actually observed increase in H/C ratio, indicating that hydrogen is getting fixed in the coal molecule probably by hydrolysis.

However, it should be pointed out that in the analysis of Run No. 11, oxygen content appears to be very high. The calculations (Appendix A) showed that increase in the O/C ratio cannot be justified by hydrolysis reaction alone.

3.2.1 Effect of Catalyst Concentration (cont'd)

Table 3.2 shows that in Run Nos. 21, 31 and 51, the amount of oxygen removal increases as the catalyst concentration decreases. This might be due to the pH of the aqueous solution of $FeSO_4$. It has been reported in the literature (6) that addition of small amounts of alkali metal compounds such as sodium hydroxide or sodium carbonate improves the oxygen removal from coal by hydrothermal treatment in presence of metal salts. Hence, the basic medium probably favours the catalytic oxygen removal by decarboxylation. In higher concentrations, the $FeSO_4$ solution might be acidic in nature, however, as the $FeSO_4$ concentration decreases, the pH of the solution increases. thereby increasing the decarboxylation reaction. On this basis, the $FeSO_4$ concentration was decreased to 0.5 g/250 ml in Run No. 221. However, in this case, the oxygen removal was negligible, suggesting a very poor catalytic activity of the aqueous solution and increased hydrolysis reaction. This indicates that certain minimum catalyst concentration is necessary for an effective catalytic activity.

In Run No. 31, where 15 g/250 ml of catalyst concentration was employed, the percentage of oxygen removal is very low. This appears to be due to experimental error. The percentage of oxygen removal was calculated based on the O/C atomic ratio of original and treated coal. The average oxygen removal for Bienfait coal is about 28%. This makes an implicit assumption that a number of carbon atoms remain constant during the treatment. This assumption may not be valid in light of the observation made about the dissolution of organic material during the blank runs, but is still good for determining oxygen removal trends.

3.2.2 Effect of Reaction Temperature

The deoxygenation runs were carried out at two different temperatures, 100°C and 150°C. The oxygen removal from the coal at 100°C was about 28%, however, at 150°C, the oxygen removal was negligible. Based on the hypothesis advanced about the reaction mechanism, it can be concluded that the rate of hydrolysis reaction, which fixes the oxygen in the coal, increases with the temperature and thereby negates the oxygen removal by decarboxylation. The H/C ratio shown in Table 3.2 for run Nos. 61, 71, 81, 91 and 101 has increased indicating a decrease in carbon atoms because of decarboxylation and increase in hydrogen atoms because of hydrolysis.

By inspection of the results of the first 11 runs, the "best" reaction temperature and catalyst concentration were determined to be 100°C and 1.6 g/250 ml respectively.

3.2.3 Effect of Different Catalysts

Table 3.3 presents the results of deoxygenation runs carried out using three different iron salts as catalysts. The salts used in the tests are $FeSO_4$, $FeCl_2$ and $Fe(OAC)_2$. The results indicate that $FeSO_4$ is the most effective catalyst followed by $Fe(OAC)_2$ and $FeCl_2$. Since the pH of the catalyst solution plays a significant role in the oxygen removal from coal, it was thought that $Fe(OAC)_2$ would be a better catalyst than $FeCl_2$. However, $FeSO_4$ turned out to be the "best" catalyst indicating that pH is not the only factor determining oxygen removal from coal. The effect of pH on the oxygen removal from coal will have to be determined in the future investigations.

Table 3.3 Deoxygenation Using Different Catalysts
Basis: Moisture Free

Run No.	Type of Coal	Catalyst	Temp. °C	Conc. of Catalyst g/250 ml	Ultimate Analysis, %						Atomic Ratio	
					Ash	C	H	N	S	O(Diff.)	O/C	H/C
51	Bienfait	$FeSO_4$	100	1.6	13.53	67.56	4.43	0.70	0.56	14.35	0.147	0.787
111	Bienfait	$FeCl_2$	100	1.6	11.47	65.45	3.78	1.30	0.65	17.34	0.199	0.693
121	Bienfait	$Fe(OAC)_2$	100	1.6	15.17	63.72	3.79	1.26	0.63	15.42	0.181	0.714

3.3 Results - Phase II

In this phase, Sundance, Forestburg and Onakawana coals representing a cross section of Canadian low rank coals were treated with the aqueous $FeSO_4$ solution at "best" temperature and two lower concentration conditions. Since the coal is a heterogenous material, it was anticipated that each coal would react differently to the deoxygenation treatment. The amount of oxygen removal at a given concentration of catalyst was different in each of the four coals.

3.3.1 Oxygen Removal Treatment for Onakawana Lignite

A total of four runs were carried out, three of which were at 100°C and one was at 150°C (Table 3.4). The result of run No. 163 in Table 3.4 shows that there is a decrease in carbon, hydrogen and oxygen content of coal in the blank run at 100°C. Calculations, made to determine the organic material lost due to the hydrothermal treatment, revealed that about 23% of organic material was dissolved in water (Appendix B for calculations). The slight reduction in oxygen content of coal may be due to the removal of hydroxyl groups because there is a drop in O/C and H/C atomic ratios. However, in run No. 173, which was carried out at 100°C and with 1.6 g/250 ml catalyst concentration, a significant increase in oxygen content of coal was recorded. The O/C atomic ratio after this run has remained the same as the blank run (No. 163) but the H/C atomic ratio has increased substantially indicating that the hydrolysis reaction dominates the decarboxylation reaction. In the run carried out at 100°C and 0.5 g/250 ml (Run No. 183), there was a significant oxygen removal which may be due to decarboxylation because of a substantial drop in the value of O/C atomic ratio.

Table 3.4 Deoxygenation Results for Onakawana Lignite
Basis: Moisture Free

Run No.	Type of Coal	Catalyst	Temp. °C	Conc. of Catalyst g/250 ml	Ultimate Analysis, %						Atomic Ratio	
					Ash	C	H	N	S	O(Diff.)	O/C	H/C
03	Onakawana	--	--	--	36.95	44.92	2.54	0.95	1.06	13.88	0.232	0.679
163	Onakawana	$FeSO_4$	100	--	43.34	40.97	2.17	0.41	0.83	12.28	0.225	0.635
173	Onakawana	$FeSO_4$	100	1.6	24.14	54.26	3.21	1.00	1.11	16.30	0.225	0.710
183	Onakawana	$FeSO_4$	100	0.5	26.70	56.12	3.26	0.91	1.30	11.85	0.158	0.697
233	Onakawana	$FeSO_4$	150	0.5	31.66	49.29	2.83	0.87	1.52	13.82	0.210	0.689

3.3.1 Oxygen Removal Treatment for Onakawana Lignite (cont'd)

In the run carried out at 150°C, there was no decrease in oxygen content of coal, though O/C atomic ratio decreased and H/C atomic ratio increased as compared to the original coal, indicating that decarboxylation and hydrolysis were occuring simultaneously. Thus, decarboxylation decreased the O/C ratio while hydrolysis reaction increased the H/C ratio and the net oxygen removal was negligible.

3.3.2 Oxygen Removal Treatment for Forestburg Coal

Table 3.5 presents the results of the deoxygenation treatment for Forestburg coal. Unlike the Bienfait and Onakawana lignite, the carbon content and the organic material content of Forestburg coal did not drop during the blank run (Run No. 194). This indicates that the humic acids in coal are not water soluble, which was expected since Forestburg coal is a higher rank coal and hence humic acid molecules must be large and complex due to the coalification process.

In the blank run at 100°C (Run No. 194), the oxygen content of coal decreased probably by decarboxylation. In this run, the O/C, and H/C decreased, indicating removal of carboxyl and hydroxyl groups from coal. However, the drop in the value of H/C was less than the drop in the value of O/C, indicating decarboxylation as a dominant reaction. When the coal was treated with $FeSO_4$ solution in the concentration of 1.6 g/250 ml at 100°C (Run No. 204), the oxygen content of coal went up as compared to the blank run. This may be due to the hydrolysis reaction because of a significant increase in the H/C atomic ratio (Table 3.5).

Table 3.5 Deoxygenation Results for Forestburg Coal
Basis: Moisture Free

Run No.	Type of Coal	Catalyst	Temp. °C	Conc.of Catalyst g/250 ml	Ultimate Analysis, %						Atomic Ratio	
					Ash	C	H	N	S	O(Diff)	O/C	H/C
04	Forestburg	-	-	-	9.50	64.00	3.90	1.70	0.60	20.30	0.238	0.731
194	Forestburg	$FeSO_4$	100	-	8.17	68.05	4.02	1.59	0.61	17.56	0.194	0.710
204	Forestburg	$FeSO_4$	100	1.6	8.44	66.13	4.06	1.82	0.53	19.02	0.216	0.737
214	Forestburg	$FeSO_4$	100	0.5	7.69	72.28	4.51	2.12	0.53	12.86	0.133	0.750
244	Forestburg	$FeSO_4$	150	0.5	9.49	70.19	4.28	2.01	0.53	13.50	0.144	0.732

3.3.2 Oxygen Removal Treatment for Forestburg Coal (cont'd)

In Run No. 214, where Forestburg coal was treated with 0.5 g/250 ml concentrated aqueous solution of $FeSO_4$ at 100°C, there was a significant drop in the oxygen content of coal. In this run, the O/C dropped while the H/C went up, indicating that oxygen removal from coal was mainly by decarboxylation. In Run No. 244, when Forestburg coal was treated with 0.5 g/250 ml concentrated, aqueous solution of $FeSO_4$ at 150°C, the oxygen removal was less than when the run was carried out at 100°C, indicating increased rate of hydrolysis reaction. Among the four Canadian coals tested at the reaction conditions employed in the experiments, Forestburg coal reacted most favourably to the oxygen removal treatment.

3.3.3 Oxygen Removal Treatment for Sundance Coal

Table 3.6 presents the results of the deoxygenation treatment for Sundance coal. In this case also, the carbon, hydrogen and oxygen contents of coal decreased after the blank run (Run No. 132). The organic material decreased by 18% per unit of ash. The organic material loss may have been caused by dissolution of humic acids in coal. The oxygen and hydrogen contents may have been produced by decarboxylation and dehydroxylation since there is a decrease in the values of O/C and H/C. In the Run Nos. 142 and 152, where the coal was treated with different concentrations of $FeSO_4$, negligible oxygen removal was attained indicating that the catalytic activities of the $FeSO_4$ solutions used in the tests were too low to obtain any additional oxygen removal above the blank run level.

3.4 Heating Value of the Treated Coal

The heating values of the original coal and the treated samples were determined by ASTM D2015 method. Table 3.7 presents the heating values of all the samples. It can be noticed from these values that the heating values of Onakawana and Sundance coal have increased significantly after the treatment, while in case of Bienfait and Forestburg coals, the heating values have not changed or decreased in few samples.

In Run No. 11, blank run with Bienfait lignite, the heating value has increased slightly because of increase in hydrogen content of coal as can be seen from H/C ratio presented in Table 3.2. However, in the subsequent experimental runs, the calorific values of samples have decreased. This may suggest a different reaction mechanism for oxygen removal. In this case, oxygen removal may by taking place by decarbonylation (removal of $>C = O$ groups) process, in which for every atom of oxygen removed, one atom of carbon is also removed and gain in heating value of coal by oxygen removal is lost due to the loss of carbon atom. Similar explanation can be given for the loss in the calorific values of Forestburg coal after the treatment. The calorific values reported for Run Nos. 71 and 91 are suspect because the amount of coal available to determine the calorific value was insufficient.

In the case of Onakawana and Sundance coals, the calorific values of the coals after the treatment increased significantly. However, the most gain in the calorific values was not observed in the samples which gave the most oxygen removal. This indicates that calorific value of the treated sample is influenced by two phenomena occurring simultaneously. They are;

1) Oxygen Removal by Decarboxylation
2) Hydrogen Fixation by Hydrolysis

Table 3.6 Deoxygenation Results for Sundance Coal
Basis: Moisture Free

Run No.	Type of Coal	Catalyst	Temp. °C	Conc. of Catalyst g/250 ml	Ultimate Analysis, %						Atomic Ratio	
					Ash	C	H	N	S	O(Diff)	O/C	H/C
02	Sundance	-	-	-	14.60	63.30	3.90	0.80	0.30	17.10	0.203	0.739
132	Sundance	$FeSO_4$	100	-	16.90	63.93	3.45	0.830	0.238	14.64	0.172	0.648
142	Sundance	$FeSO_4$	100	1.6	17.85	63.03	3.26	1.275	0.210	14.38	0.171	0.621
152	Sundance	$FeSO_4$	100	0.5	15.38	63.75	3.61	1.40	0.06	15.8	0.186	0.680

Table 3.7 Heating Values of Coal and Treated Samples

Run No.	Coal	Catalyst	Concentration g/250 ml	Temperature °C	Heating Values Dry J/g
01	Bienfait	None	N/A	N/A	22323
11	Bienfait	None	Blank	100	23435
21	Bienfait	$FeSO_4$	50	100	22205
31	Bienfait	$FeSO_4$	15	100	22449
41	Bienfait	$FeSO_4$	5	100	--
51	Bienfait	$FeSO_4$	1.6	100	22753
221	Bienfait	$FeSO_4$	0.5	100	23277
61	Bienfait	None	Blank	150	21835
71	Bienfait	$FeSO_4$	50	150	20667 *
81	Bienfait	$FeSO_4$	15	150	21798
91	Bienfait	$FeSO_4$	5	150	20207 *
101	Bienfait	$FeSO_4$	1.6	150	22570
111	Bienfait	$FeCl_2$	1.6	100	21058
121	Bienfait	$Fe(OAC)_2$	1.6	100	21732
02	Sundance	None	N/A	N/A	20860
132	Sundance	None	Blank	100	21860
142	Sundance	$FeSO_4$	1.6	100	22672
152	Sundance	$FeSO_4$	0.5	100	24439
03	Onakawana	None	N/A	N/A	13535
163	Onakawana	None	Blank	100	17818
173	Onakawana	$FeSO_4$	1.6	100	19563
183	Onakawana	$FeSO_4$	0.5	100	18793
233	Onakawana	$FeSO_4$	0.5	150	18058
04	Forestburg	None	N/A	N/A	25546
194	Forestburg	None	Blank	100	25223
204	Forestburg	$FeSO_4$	1.6	100	25330 *
214	Forestburg	$FeSO_4$	0.5	100	24600
244	Forestburg	$FeSO_4$	0.5	150	23942

* Sample quantity not sufficient for analysis.

3.4 Heating Value of the Treated Coal (cont'd)

It can be observed in Run No. 173, that the ratio of the O/C has remained the same as that of blank run (163) indicating decarboxylation reaction but H/C has increased substantially indicating hydrogen fixation and hence the calorific value has gone up significantly. Similarly in Run No. 152 of Sundance coal, the gain in the calorific value is higher than for sample of Run No. 142.

However, in the case of Onakawana lignite, it can be noticed from Table 3.4 that ash content of coal is appreciably lower for the treated samples in Run Nos. 173 and 183. The ash content has been reduced by about 33%. This may be due to removal of magnesium and calcium ions in the ash by formation of their sulphate salts which are soluble in water. Hence, in this case the increase in heating value of coal cannot be attributed only to oxygen removal. Part of the increase is due to ash removal. This discovery may lead to a development of coal beneficiation process, which would remove ash and oxygen simultaneously from coal. This approach is recommended for the future project.

To determine the effect of catalyst concentration on the heating value of the treated coal, the heating values of all four different Canadian coals and their treated samples were plotted against the catalyst concentration in Figure 3.1. No general trend was observed for the variation of heating value with catalyst concentration. Hence to understand the phenomenon better, the percent increase in the heating value of coal after treatment was plotted against the heating value of the original coal in Figure 3.2. This figure clearly indicates that lower the original heating value of coal, higher the resulting increase in the heating value of the treated sample. This indicates that process has a great value in terms of beneficiating lower rank coals such as Onakawana lignite, where the gain in heating value is the highest after the treatment.

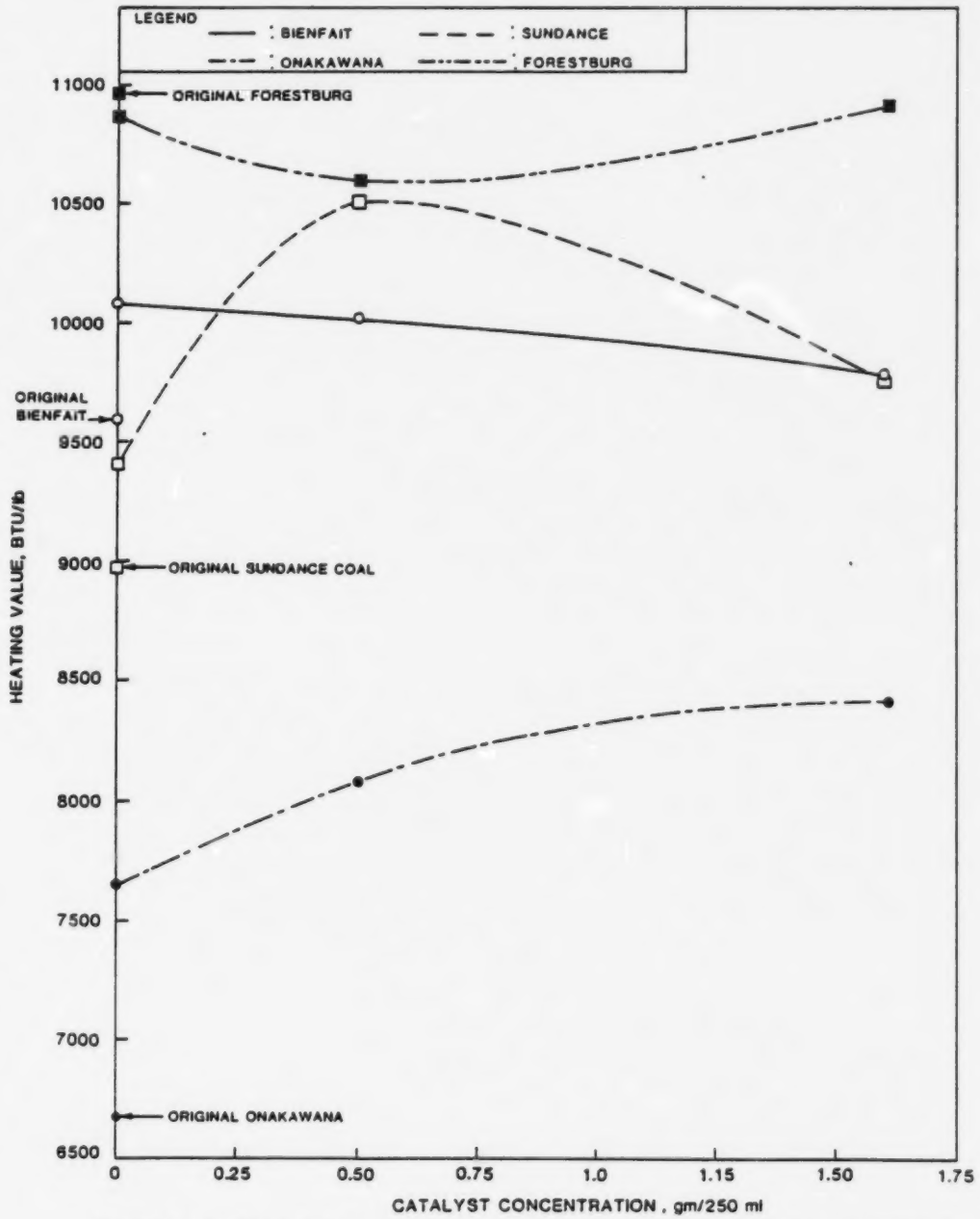

FIGURE 3.1 PLOT OF CATALYST CONCENTRATION V_s BTU VALUES OF FOUR CANADIAN COALS

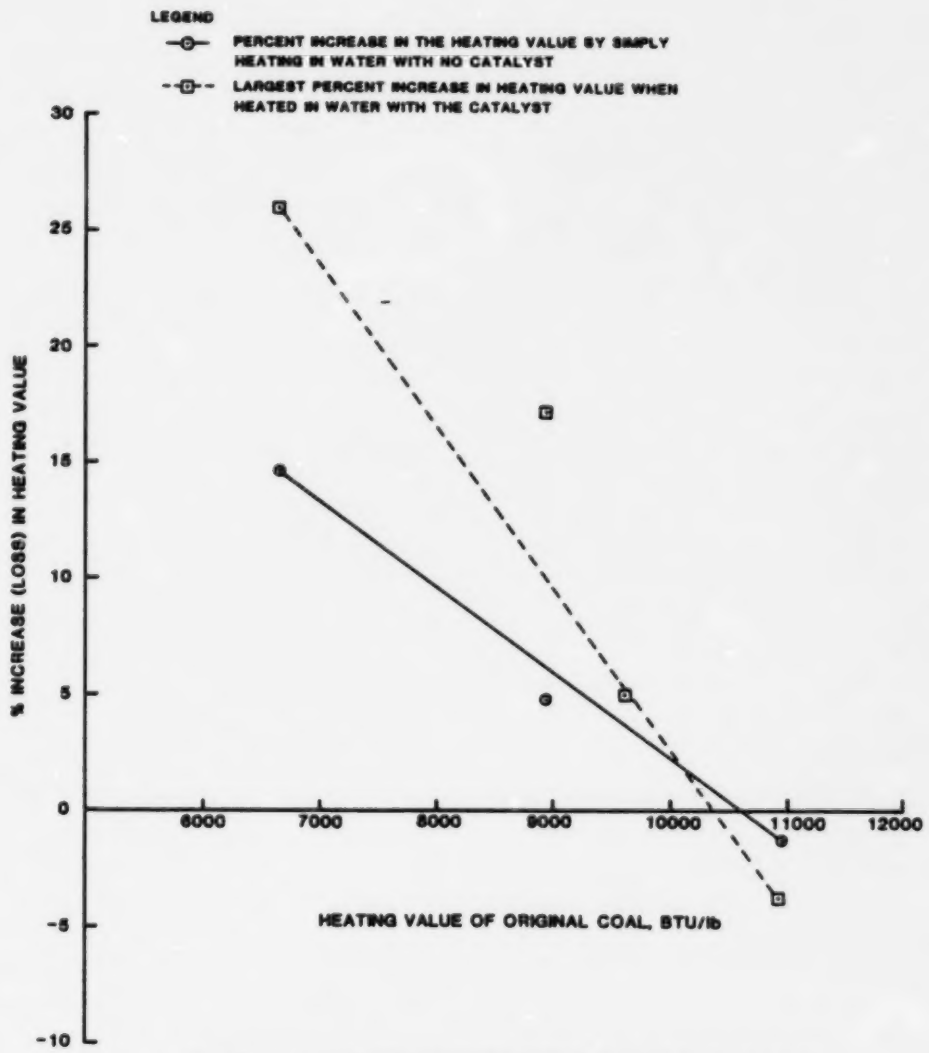

FIGURE 3.2 PLOT OF PERECENT INCREASE IN HEATING VALUE OF COAL Vs HEATING VALUE OF ORIGINAL COAL

3.4 Heating Value of the Treated Coal (cont'd)

To show the trend of the increase in heating value of treated coal with the variation in the catalyst concentration, the catalyst concentration at maximum increases in heating value of coal was plotted against the original heating value of coal in Figure 3.3. The catalyst concentration to achieve the maximum increase in the heating value was highest for the lowest rank coal and it decreased as the rank of coal increased.

Based on this observation, it is hypothesized that, $FeSO_4$ catalytically attacks the carboxyl goups first during the treatment. Once all the carboxyl groups (-COOH group) are removed from the coal, the remaining "active" $FeSO_4$ catalyst, decomposes the other oxygen functionality in coal, such as carbonyl groups. As mentioned earlier in the report that the carbonyl groups may be removed from coal in the case of Bienfait lignite and Forestburg coal. It is known that lower rank coals have higher amounts of carboxyl groups, hence they require higher catalyst concentration to remove the carboxyl groups and to achieve maximum increase in the heating value. Once the carbonyl groups start to decompose the heating value of treated sample drops.

To check the consistency of the calorific values determined, heating value for each sample was determined using the ultimate analysis and Dulong's formula. The values determined experimentally were plotted against the heating values found by using Dulong's formula in Figure 3.4. For most of the samples the predicted heating values were higher than the experimentally determined values, indicating either experimental error or weathering of the treated sample during the storage.

The gain in the heating values of the treated coals were converted to the gain in the dollar value of coal in terms of dollars per tonne of coal. These values for Sundance coal and Onakawana lignite are presented in Table 3.8. The value of $1 per million BTU was assumed to be the

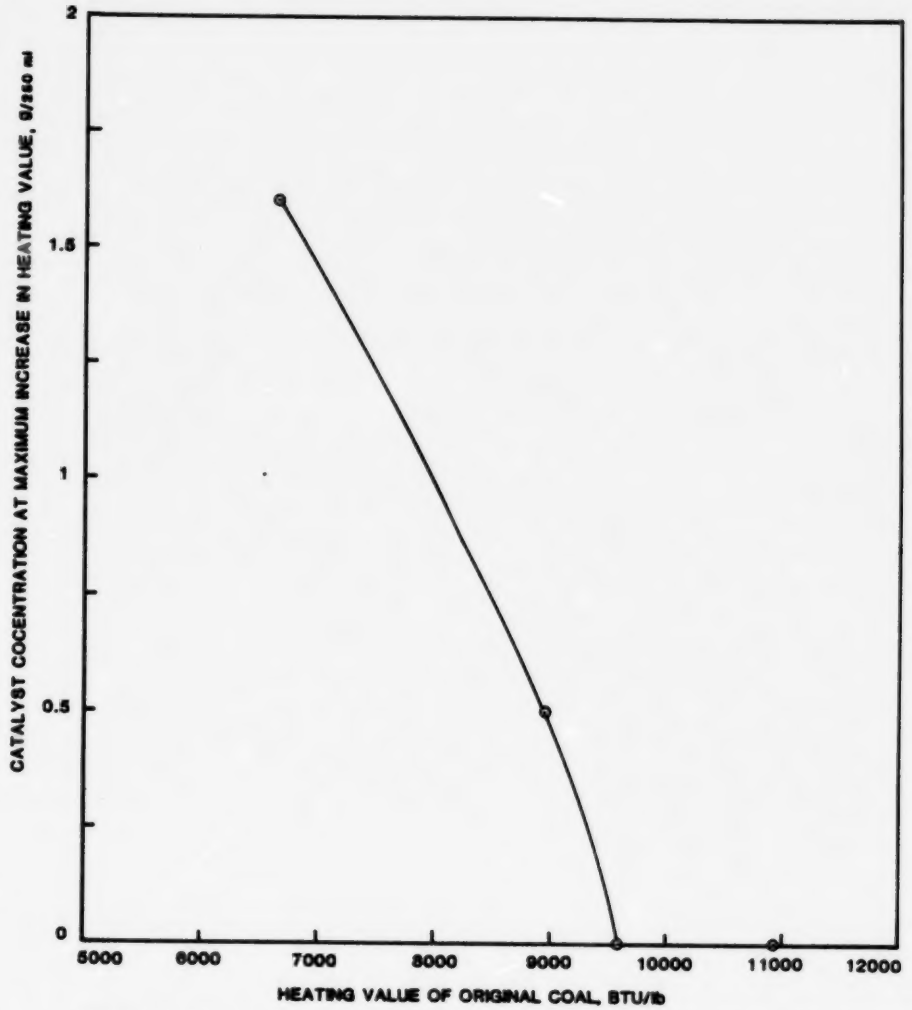

FIGURE 3.3 PLOT OF CATALYST CONCENTRATION AT MAXIMUM INCREASE IN HEATING VALUE Vs THE HEATING VALUE OF ORIGINAL COAL

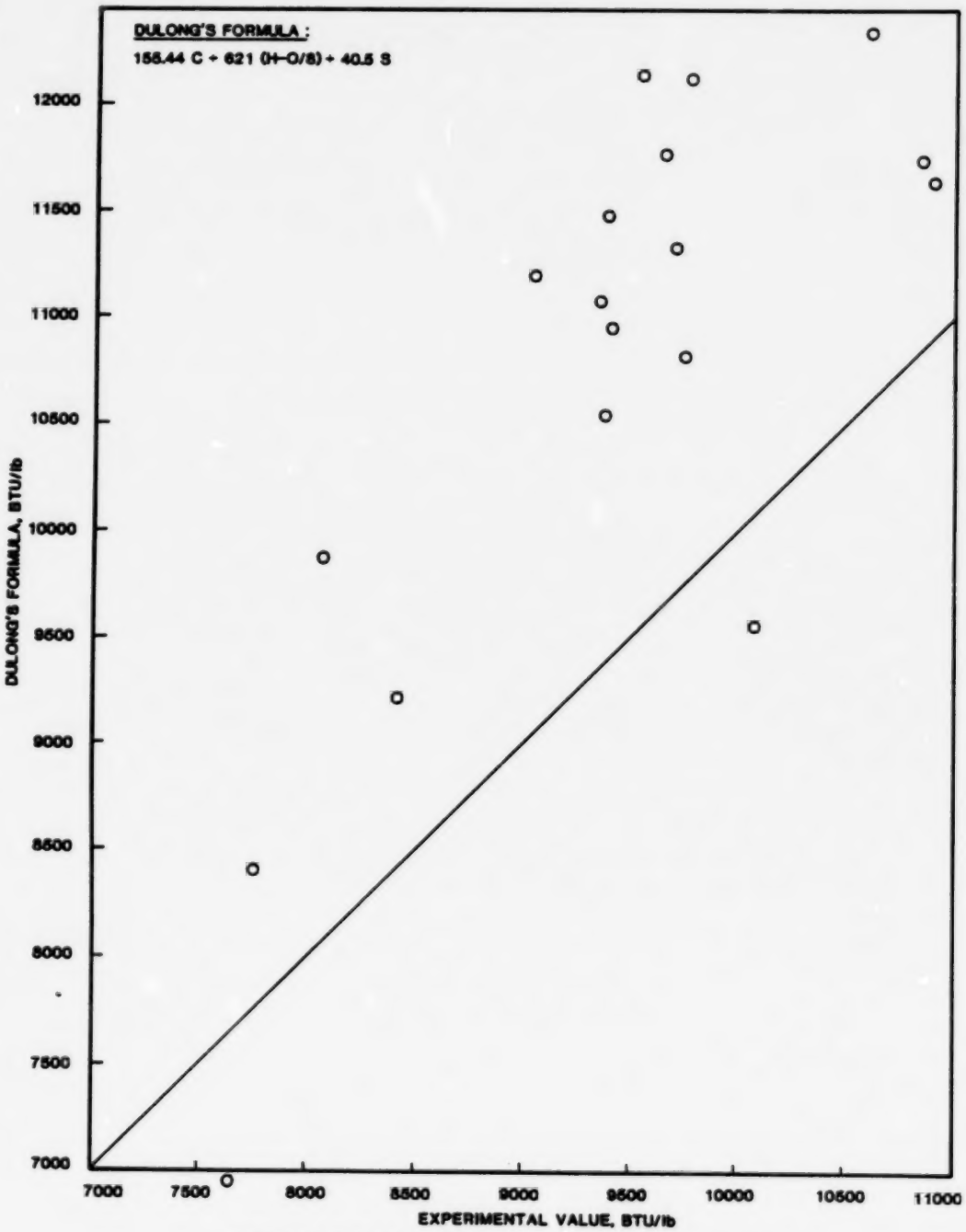

FIGURE 3.4 PLOT OF EXPERIMENTALLY DETERMINED BTU VALUE V_B.
BTU VALUES DETERMINED USING DULONG'S FORMULA

Table 3.8 Value Appreciation of Treated Coal

Basis: $\$1/10^6$ Btu

Run No.	Coal	Calorific Value Before the Treatment Btu/lb	Calorific Value After the Treatment Btu/lb	Gain in Calorific Value Btu/lb	Gain in Value of Coal $/Tonne
163	Onakawana	6680	7662	982	2.16
173	Onakawana	6680	8413	1733	3.82
183	Onakawana	6680	8081	1401	3.10
132	Sundance	8970	9400	430	0.95
142	Sundance	8970	9749	779	1.72
152	Sundance	8970	10509	1539	3.39

3.4 Heating Value of the Treated Coal (cont'd)

basis for the calculations. The value of Onakawana lignite increased by as much as $3.82 per tonne of coal, while the value of Sundance coal increased by about $3.39 per tonne of coal.

4.0 CONCLUSIONS

The following conclusions can be drawn from the present investigation. It should be pointed out that the amount of work done in the present investigation was modest. Based on these data, certain conclusions have been drawn, which are presented below. Some of these conclusions may have stretched the limits of the accuracy and predictability of the analysis. Nevertheless, the observations are consistent with what is known about the structure of coal.

1. Low rank coals (Bienfait, Onakawana and Sundance coal) lose as much as 20% organic material when they are heated in water at 100°C. This loss is probably caused by the dissolution of humic acids in water. No such loss was observed in the case of subbituminous coal (Forestburg).

2. Iron salts used as catalysts remove oxygen from all the four coals tested.

3. The oxygen removal from Bienfait lignite was higher when it was treated at temperature of 100°C than when it was treated at 150°C.

4. The amount of oxygen removal at a given reaction condition was different for different coals. The amount of oxygen removed varied with type of coal.

5. $FeSO_4$ was the most effective catalyst followed by $Fe(OAC)_2$ and $FeCl_2$ respectively in terms of their catalytic activity.

6. The dilute solutions of $FeSO_4$ (1.6 g/250 ml) had better catalytic activity for the oxygen removal than the concentrated solutions (50 g/250 ml, 15 g/250 ml, 5 g/250 ml) for Bienfait lignite. However, the most effective concentration of catalyst solution was different for different coals.

4.0 CONCLUSIONS (cont'd)

7. When Bienfait coal was heated to 100°C in water (blank), its oxygen content probably increased by hydrolysis. However, in the other three coals, namely, Forestburg, Sundance and Onakawana, the oxygen content of coal decrease when they were heated to 100°C in water (blank) may be due to decarboxylation.

8. The heating value of Onakawana and Sundance coal samples increased significantly after the hydrothermal treatment, while for, Bienfait lignite and Forestburg coal the heating values remained the same or decreased slightly.

5.0 RECOMMENDATIONS FOR FURTHER WORK

The following recommendations are made:

1. The precise influence of the pH of the medium on the catalytic deoxygenation of coal should be determined. This can be done by varying the pH of the aqueous $FeSO_4$ solution by adding varying quantities of NaOH or Na_2CO_3. A number of runs should be made to determine the correlation between the decarboxylation reaction and the pH and the influence of hydrolysis reaction on the net oxygen removal from coal.

2. The content and composition of ash in coal might be having some effect on the catalytic decarboxylation of coal. Hence, coal with different ash contents and different ash compositions should be tested to determine the relationship between ash content and composition and oxygen removal from coal.

3. It was established in this investigation that each coal reacts differently to the deoxygenation treatment at given process conditions. This indicates that for each coal, the "best" process conditions should be established individually. Hence, a number of Canadian coals should be tested under varying operating conditions in order to establish the "best" operating conditions for each Canadian coal.

4. It has been reported that iron catalytically increases the coal liquefaction yield and in the present investigation, it has been established that $FeSO_4$ catalytically removes oxygen from coal. Thus, a two-step process can be developed in which the first step would be a coal beneficiation by treating coal with $FeSO_4$ to reduce its oxygen content and the second step would be a coal liquefaction in presence of $FeSO_4$. This would reduce the costly hydrogen consumption and improve the liquefaction yields.

5.0 RECOMMENDATIONS FOR FURTHER WORK (cont'd)

5. A detailed reaction mechanism study should be carried out employing number of model compounds such as organic aliphatic acids, organic aromatic acids and dibasic acids. Since coal is a mixture of large number of compounds, the phenomenon of catalytic deoxygenation will have to be understood using model compounds. Also the analytical method to determine oxygen will have to be refined, so that oxygen will not have to be determined by difference. The better understanding of the reaction mechanism would enable us to predict the catalytic deoxygenation effect of $FeSO_4$ on different coals.

6. A conceptual process design and the techno-economic assessment of the coal beneficiation process by utilizing $FeSO_4$ as a catalyst should be carried out.

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APPENDIX A

CALCULATIONS TO EVALUATE THE
REACTION MECHANISM HYPOTHESIS

Oxygen removal by decarboxylation from coal results in evolution of CO_2 and therefore decrease in oxygen and carbon atoms of the coal. Hence, if decarboxylation is taking place, the H/C ratio of the treated material should be greater than the H/C ratio of the original coal. Moreover, if hydrolysis is taking place, then H/C ratio should be further increased.

Determination of the loss of carbon atoms due to decarboxylation reaction, on the assumption that no hydrolysis is taking place.

Basis: 100 carbon atoms

O/C ratio in feed coal = 0.231

O/C ratio after run no. 21 = 0.164

Let X molecules of carboxyl groups (-COOH) are removed in the run

Let Y be the ratio of O to C atoms after the run

Let Z be the atomic ratio of H/C after the run

Hence, for X molecule of -COOH removed,

2X atoms of oxygen are removed and

X atoms of carbon are removed

$\therefore$ By oxygen balance

$$\frac{23.1 - 2X}{100 - X} = Y$$

$$\therefore 23.1 - 2X = 100Y - XY$$

$$\therefore 23.1 - 100Y = 2X - XY$$

$$\boxed{X = \frac{23.1 - 100Y}{2 - Y}} \qquad (1)$$

∴ Now by hydrogen balance

$$\frac{71.4}{100 - X} = Z$$

$$\boxed{X = 100 - \frac{71.4}{Z}} \qquad \text{(2)}$$

The value X determined by (1) and (2) should be the same, if not, then assume that hydrolysis is taking place.

∴ Hydrogen Balance based on the assumption that hydrolysis is taking place.

$$\boxed{\frac{71.4 + n}{100 - X} = Z} \qquad \text{(3)}$$

where n/2 number of ester groups hydrolysed

∴ By Oxygen Balance

$$\boxed{\frac{23.1 - 2X + n/2}{100 - X} = Y} \qquad \text{(4)}$$

This results in two equations and two unknowns.

When the value of X determined by equation 2 is larger than the value of X determined by eq. 1, it can be concluded that hydrolysis taking place.

Example : Run No. 21

O/C atomic ratio of feed coal = 0.231
O/C atomic ratio after run no. 21 = 0.164
H/C atomic ratio after run no. 21 = 0.777

Now by equation 1 for oxygen balance

$$X = \frac{23.1 - 100Y}{2 - Y}$$

$$= \frac{23.1 - 16.4}{- 0.164}$$

$$X = 6.7/1.836 = 3.65$$

$$\boxed{X = 3.65} \qquad (5)$$

Now by hydrogen balance, equation 2

$$X = 100 - \frac{71.4}{0.777}$$

$$\boxed{X = 8.11} \qquad (6)$$

The equation 6 indicates that to justify the rise in the H/C atomic ratio observed experimentally, there should have been a loss of 8.11 carboxyl groups/100 carbon atoms. The loss of carboxyl groups calculated by the decrease in O/C atomic ratio is 3.65 which indicates the hydrogen fixation in coal molecule by hydrolysis.

The number of molecules of water added to coal molecule by hydrolysis can be calculated by equation 3 and 4

By Hydrogen Balance

$$\therefore \frac{71.4 + n}{100 - X} = 0.777$$

$$\boxed{n + 0.777X = 6.3} \qquad (7)$$

By Oxygen Balance

$$\frac{23.1 - 2X + n/2}{100 - X} = 0.164$$

$$\boxed{n - 3.672X = 13.4} \qquad (8)$$

Solving equations 7 and 8 simultaneously.

$$\boxed{X = 4.428}$$

$$n = 2.86$$

$$\boxed{\text{Molecules of water added} = n/2 = 1.43}$$

Similar calculations were made for all the runs.

APPENDIX B

CALCULATIONS TO DETERMINE THE LOSS OF ORGANIC MATERIAL DURING BLANK RUNS

Case I Bienfait Lignite

Assuming that ash is not affected during the blank runs.

Basis: 100 units of coal

∴ Original coal has 11.88% ash and 88.12% organic matter (Table 3.1)

∴ Water treated coal has 12.86% ash and 87.14% organic matter (Run No. 11, Table 3.2).

∴ Amount of coal substance expected after the treatment if none dissolved

$$\frac{12.86}{11.88} \quad (88.12) = 95.39$$

However, only 87.14 units were associated with the 12.86 parts of ash

$$\text{Missing organic matter} = \frac{95.39 - 87.14}{12.86}$$

$$= 0.6415/\text{unit of ash}$$

Therefore

$$\frac{88.12}{11.88} = 7.42 \text{ units of organic/ash in original coal}$$

$$\therefore \% \text{ lignite dissolving} = \frac{0.64}{7.42} \times 100 = 8.63\%$$

Case II Onakawana Lignite

Basis: 100 units of coal

∴Original coal has 36.95% ash and 63.05% coal matter (Table 3.1).

∴Water treated coal has 43.34% ash and 56.66% coal matter.

∴Amount of organic substance expected after reaction if none dissolve

$$\frac{43.34}{36.95} \times 63.05 = 73.95$$

However, only 56.66 units were associated with the 43.34 parts of ash.

$$\text{Missing organic matter} = \frac{73.95 - 56.66}{43.34}$$

$$= 0.3989$$

Now, we have

$$\frac{63.05}{36.95} = 1.706 \quad \text{units of organic/ash in original coal}$$

$$\therefore \text{ \% lignite dissolving} = \frac{0.3989}{1.706} = 23.38$$

Case III Sundance Coal

Basis: 100 units of coal

∴Original coal has 14.6% ash and 85.4% coal matter (Table 3.1)

∴Water treated coal has 16.9% ash and 83.1% coal matter (Table 3.1)

∴Amount of organic substance expected after reaction if none dissolved

$$\frac{16.9}{14.6} \times 85.4 = 98.85$$

However, only 83.1 units were associated with the 16.9 parts of ash

$$\text{Missing organic matter} = \frac{98.95 - 83.1}{16.9}$$

$$= 0.9379$$

Now, we have

85.4/14.6 = 5.8493 units of organic/ash in original coal

$$\text{\% lignite dissolving} = \frac{0.9379}{5.8493} = 16.03\%$$